UNIT 4

CHEMICAL KINETICS

CONCEPT

Chemical Kinetics : The branch of physical chemistry which deals with the study of rate of reaction and factors affecting rate.

Rate of chemical reaction : The change in concentration of any reactant or product per unit time is called rate of reaction.

Types of Rate of Reaction :

1. **Average rate of reaction :** The rate of reaction measured over the long time interval is called average rate of reaction.

$$\text{Avg rate } \Delta x/\Delta t = -\Delta[R]/\Delta t = +\Delta\,[p]/\Delta t$$

2. **Instantaneous rate of reaction :** The rate of reaction measured at a particular time is called instantaneous rate of reaction.

$$(\text{Rate})_i = (\text{Instantaeous rate})\ dx/dt = -d[R]/dt = +d[P]/dt$$

Factors affecting Rate of Reaction

1. Concentration of reactant
2. Surface area
3. Temperature
4. Nature of reactant
5. Presence of catalyst
6. Radiation in photochemical reaction

Rate constant (k) : It is equal to the rate of reaction when molecular concentration of reactant is at unity.

Rate law : The rate of reaction is directly proportional to the product of concentration of reactant and each concentration is raised to some power which may or may not be equal to stereochemistry experimentally.

For a reaction, $aA + bB \rightarrow cC + dD$

$$\text{Rate law} = k[A]^p[B]^q$$

where powers p and q are determined experimentally.

Molecularity : The total number of reactants taking part in elementary chemical reaction is called molecularity.

Order of reaction : The sum of powers to which the concentration terms are raised in a rate law expression is called order of reaction.

For above case, Order = P + Q

Orders of reaction is determined experimentally.

Half-life period : The time during which the concentration of the reactant is reduced to half of its initial concentration is called half-life period.

Activation energy : The minimum extra amount of energy absorbed by reactant molecules so that their energy becomes equal to the threshold energy is called activation energy.

Activation energy = Threshold energy – Kinetic energy

Temperature coefficient : The ratio of rate constant at two temperatures having difference of 10ºC is called temperature coefficient.

Temperature coefficient = Rate constant at T + 10ºC/Rate constant at TºC

Arhenius Equation :

$$K = Ae^{-Ea/RT}$$

where, K = Rate constant

A = Arrhenius energy (Frequency factor or pre-exponential factor)

E_a = Activation energy

R = Rate constant

T = Temperature

$\frac{Ea}{RT}$ = Fraction of molecules having energy equal to or more than activation energy

$$\text{Log } K = \text{Log } A - \frac{Ea}{2.303RT}$$

$$\text{Log } \frac{K_2}{K_1} = \frac{Ea}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Enery of activation can be evaluated as :

$\text{Log}[K2/K1] = Ea\ (1/T1-1/T2)/2.303RT$

$\text{Log}[K2/K1] = Ea(1/T1-1/T2)\ /\ 19.15$

1. Integrated rate law equation for zero order reaction is given as below :

(a) $k = \dfrac{[R]_o\ \ [R]_t}{t}$

Where k is rate constant and $[R]_0$ is initial molar concentration.

(b) $t_{1/2} = \dfrac{[R]_o}{2k}$ $t_{1/2}$ is half-life period of zero order reaction.

2. Integrated rate law equation for first order reaction :

(a) $k = \dfrac{2.303}{t} \log \dfrac{[R]_\circ}{[R]_t}$

where k is rate constant, $[R]_0$ is initial molar concentration and [R] is final concentration at time 't'.

(b) Half-life period ($t_{1/2}$) for first order reaction :

$$t_{½} = \frac{0.693}{k}$$

Pseudo chemical reaction : The chemical reaction which looks like higher order reaction but in real it follows lower order reaction.

$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$$

$\text{Rate} = k[CH_3COOC_2H_5]^1$

Order = 1

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. The gas phase decomposition of acetaldehyde

$$\mathbf{CH_3CHO \rightarrow CH_4 + CO}$$

follows the rate law, Rate = $k(P_{CH3CHO})^{3/2}$, unit of P is atm and time is second.

What are the units of its rate constant ?

Ans. $Atm^{-½}\ sec^{-1}$

Q. 2. State the order with respect to each reactant and overall reaction.

$$\mathbf{H_2O + 3I^- + 2H^+ \rightarrow 2H_2O + I^{3-}}$$

Rate = $k[H_2O_2]^1[I^-]^1$

Ans. Order of reaction = 1 + 1 = 2

Q. 3. Give one example of pseudo first order reaction.

Ans. Hydrolysis of an ester :

$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$$

Q. 4. The rate law for a reaction is

Rate = K [A] $[B]^{3/2}$

Can the reaction be an elementary process ? Explain.

Ans. No, an elementary process would have a rate law with orders equal to its molecularities and therefore must be in integral form.

Q. 5. For the reaction $3H_2 + N_2 \rightarrow 2NH_3$, how are the rate of reaction expressions $-\frac{d[H_2]}{dt}$ and $\frac{d[NH_3]}{dt}$ inter-related ?

Ans. $-\frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$

Q. 6. Identify the order of a reaction from the following rate constant :

$k = 2.3 \times 10^{-5}$ L mol^{-1} s^{-1}

Ans. Second order

Q. 7. After five half-life periods for a first order reaction, what fraction of reactant remains ?

Ans. $\frac{1}{32}$

Q. 8. Give the damaging effect of photochemistry.

Ans. The colour of fabrics fades away on exposure to sunlight.

Q. 9. What is the effect of adding catalyst on the free energy of a reaction ?

Ans. No change in ΔG.

Q.10. What value of *k* is predicted for the rate constant by Arrhenius equation is T $\rightarrow \infty$? Is this value physically reasonable ?

Ans. From the equation $k = Ae^{-E_a/RT}$ if T $\rightarrow \infty$ $k \rightarrow$ A so that Ea = 0. This is not feasible.

Q.11. Determine the order of reaction :

Step 1.	**$2NO + H_2 \rightarrow N_2 + H_2O_2$**	**Slow**
Step 2.	**$H_2O_2 + H_2 \rightarrow 2H_2O$**	**Fast**

Ans. Rate $= k\,[NO]^2\,[H_2]$

Order $= 2 + 1$

$= 3$

Q.12. What is the order of reaction whose rate constant has the same units as the rate of reaction ?

Ans. Zero order

Q.13. Why are reactions of higher order less in number ?

Ans. A reaction takes place due to collide of molecules. The chances for a large number of molecules or ions to collide simultaneously are less. Hence, the reactions of higher order are less.

Q.14. What will be the effect of temperature on rate constant ?

Ans. Rate constant of a reaction is nearly doubled with rise in temperature by 10º.

Q.15. State a condition under which a bimolecular reaction is kinetically first order reaction.

Ans. A bimolecular reaction becomes first order reaction when one of the reactants is in excess.

Q.16. Why can't molecularity of any reaction be equal to zero ?

Ans. Molecularity of a reaction means the number of molecules of the reactants taking place in an elementary reaction. Since at least one molecule must be present, so that molecularity will be atleast one.

Q.17. Give an example of zero order reaction.

Ans. $H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$ or any other example

Q.18. The rate constant of a reaction is 3×10^2 min^{-1}. What is its order of reaction ? (On the basis of units of rate constant)

Ans. First order reaction.

Q.19. Three-fourth of a reaction is completed in 32 minutes. What is the half life period of this reaction ?

Ans. 16 minutes.

Q.20. What is meant by an elementary reaction ?

Ans. A reaction which takes place in one step is called an elementary reaction. For example : $H_2 + I_2 \rightarrow 2HI$.

Q.21. Give one example of a reaction where order and molecularity are equal ?

Ans. $2HI \rightarrow H_2 + I_2$ (Order = Molecularity = 2)

Q.22. For a reaction R → P, the rate becomes 2 times when the concentration of the reactant A is increased 4 times. What is the order of reaction ?

Ans. $r = k(a)^n \Rightarrow 2r = k(4a)^n \Rightarrow 2 = 4^n \Rightarrow n = 0.5$

Q.23. The rate constant of a zero order reaction in A is 0.003 mol L^{-1} sec^{-1}. How long will it take for the initial concentration of A to fall from 0.10M to 0.075 M ?

Ans. $t = \dfrac{[A]_0 - [A]}{k} = \dfrac{0.10 - 0.075}{0.003} = 8.3 \text{ sec}$

Q.24. In a reaction 2A → Products, the concentration of A decreases from 0.5 mol L^{-1} in 10 minutes. Calculate the rate during this interval.

Ans. Average rate $= \dfrac{-\Delta[A]}{2\Delta t} = -\dfrac{1}{2}\left(\dfrac{0.4 - 0.5}{10}\right) = 5 \times 10^{-3} \text{ M min}^{-1}$

Q.25. In some cases large number of colliding reactant molecules have energy more than threshold energy even then the reaction is slow. Why ?

Ans. Because resultant molecules do not collide in proper orientation.

Q.26. Give an example of a reaction having fractional order.

Ans. Decomposition of acetaldehyde (order = 1.5).

$$CH_3CHO \xrightarrow{723K} CH_4 + CO$$

Q.27. Decomposition reaction of ammonia on 1*t* surface has rate constant = 2.5 × 10^{-1} mol L^{-1} sec^{-1}. What is order of reaction ?

Ans. Unit of *k* explain that it is zero order reaction.

Q.28. What is order of radioactive decay ?

Ans. First order

Q.29. For a reaction A + B → Product, the rate low is given by $r = k[A]^{½}[B]^2$. What is the order of the reaction ?

Ans. Order of reaction = ½ + 2 = 2.5

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Q. 1. The rate of a particular reaction quadruples when the temperature changes from 293 K to 313 K. Calculate activation energy.

Ans. $K_2/K_1 = 4$

$T_1 = 293$ K, $T_2 = 313$ K

$$\log\frac{K_2}{K_1} = -\frac{E_a}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

Thus, on calculating and substituting values, we get :

$E_a = 52.86$ KJ mol^{-1}

Q. 2. If the decomposition of nitrogen oxide as

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

follows a first order kinetics.

(a) Calculate the rate constant for a 0.05M solution if the instantaneous rate is 1.5×10^{-6} mol/l/s ?

Ans. $\text{Rate} = K[N_2O_5]$

$$K = \frac{\text{Rate}}{[N_2O_5]}$$

$$= \frac{1.5 \times 10^{-6}}{0.05}$$

$$K = 3.0 \times 10^{-5}$$

(b) What concentration of N_2O_5 would give a rate of 2.45×10^{-5} mol L^{-1} s^{-1} ?

Ans. $\text{Rate} = 2.45 \times 10^{-5}$ mol L^{-1} s^{-1}

$$[N_2O_5] = \frac{\text{Rate}}{K} = \frac{2.45 \times 10^{-5}}{3.0 \times 10^{-5}}$$

$$= 0.82 \text{ M}$$

Q. 3. Write the difference between order and molecularity of reaction.

Ans.

Order	Molecularity
1. It is the sum of the powers of concentration terms in the rate law expression.	It is the number of reacting species undergoing simultaneously collision in a reaction.
2. It is determined experimentally.	2. It is a theoretical concept.
3. Order of reaction need not to be a whole number.	3. It is whole number only.
4. Order of reaction can be zero.	4. It can't be zero or fractional.

Q. 4. The rate constant for a reaction of zero order A is 0.0030 mol L^{-1} s^{-1}. How long will it take for the initial conc. of A to fall from 0.10M to 0.075M ?

Ans. For a zero order reaction,

$$K = 0.0030 \text{ mol } L^{-1} s^{-1}$$

$$[A]_0 = 0.10M \qquad [A] = 0.075M$$

$$K = \frac{[A]_0 - [A]}{t}$$

$$t = \frac{0.10 - 0.075}{0.0030} = 8.33 \text{ s}$$

Q. 5. For the reaction :

Write : $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$

(a) Rate of reaction expression.

(b) Molecularity

Ans. (a) $\text{Rate} = -\frac{d[C_{12}H_{22}O_{11}]}{dt} = -\frac{d(H_2O)}{dt}$

$$= \frac{d[C_6H_{12}O_6]}{dt} = \frac{d[C_6H_{12}O_6]}{dt}$$

(b) Molecularity = 2

Q. 6. Consider the decomposition reaction :

$$2H_2O_2 \xrightarrow{OH^-/I^-} 2H_2O + O_2$$

This reaction takes place in two steps as given below :

Step 1. $H_2O_2 + I^- \rightarrow H_2O + IO^-$ **(slow)**

Step 2. $H_2O_2 + IO^- \rightarrow H_2O + I^- + O_2$ **(fast)**

(a) Determine rate law expression.

(b) Determine the order of reaction.

Ans. (a) Rate = $K[H_2O_2][I^-]$ because second step is rate determining step.

(b) Order = 1 + 1 = 2

Q. 7. The decomposition of hydrocarbon follows the equation $K = (4.5 \times 10^{11} \text{ s}^{-1}) e^{-28000k/T}$. Calculate E_a.

Ans. $K = (4.5 \times 10^{11} \text{ s}^{-1}) e^{-28000k/T}$

Comparing the equation with Arrhenius equation,

$$K = Ae^{-Ea/RT}$$

$$-\frac{E_a}{R} = -28000\ K$$

$$E_a = 28000 \times 8.314$$

$$= 232192\ J\ mol^{-1}$$

Q. 8. For a reversible reaction,

$$H_2 + I_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2HI$$

derive an expression for the formation of HI.

Ans. Rate of reaction $= \frac{1}{2}\frac{d[HI]}{dt}$

$$= k_1[H_2]\,[I_2] - 2k_2[HI]^2$$

Rate of formation of HI $= 2k_1[H_2]\,[I_2] - 2k_2[HI]^2$

Q. 9. A reaction is of second order with respect to a reactant. How is the rate of reaction affected if the conc. of the reactant is reduced to half. What is the unit of rate constant for such a reaction ?

Ans. Rate $= k[A]^2$

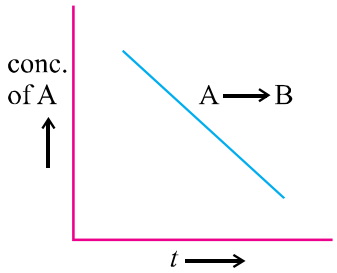
$$\text{Unit of } k = \frac{\text{mol L}^{-1}}{S} = k(\text{mol}^{-1})^2$$

$$k = \text{mol}^{-1}\ L\ S^{-1}$$

Q.10. For a first order reaction time taken for half of the reaction to complete is t_1 and ¾ of the reaction to complete is t_2. How are t_1 and t_2 related ?

Ans. $t_2 = 2t_1$ because for 3/4th of the reaction to complete time required is equal to two half lives.

Q. 11.



(a) What is the order of the reaction ?

(b) What is the slope of the curve ?

Ans. (a) Zero order reaction.

(b) $[R] = [R_0] - kt$

$\therefore$ Slope = $-k$

Q.12. Derive an expression to calculate time required for completion of zero order reaction.

Ans. For a zero order reaction,

$$R = [R]_0 - kt$$

For completion of the reaction [R] =0

$\therefore \quad kt = [R]_0$

Or $$t = \frac{[R]_0}{k}$$

Q.13. For the reaction N_2 (g) + $3H_2$ (g) $\rightarrow$ $2NH_3$ (g)

How is the rate of formation of ammonia related to the rate of disappearance of H_2 ?

Ans. Rate of reaction $$= -\frac{1}{3}\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$$

Or $$\frac{\Delta[NH_3]}{\Delta t} = -\frac{2}{3}\frac{\Delta[H_2]}{\Delta t}$$

Q.14. The rate of a gaseous reaction becomes half when volume of the vessel is doubled. What is the order of reaction ?

Ans. Suppose, order of reaction is *n* and the reaction is A (g) $\rightarrow$ Products

$$\text{Rate} = k[A]^n \qquad ...(i)$$

When volume is doubled, molar conc. becomes half and rate of reaction gets halved.

$$\frac{\text{Rate}}{2} = k\left(\frac{A}{2}\right)^n \qquad ...(ii)$$

Dividing equation (i) by equation (ii),

$$(2)^1 = (2)^n$$

Or $$n = 1$$

Q.15. A reaction which is first order with respect to A has rate constant 6 min^{-1}. If we start with [A] = 0.5 mol L^{-1}, when would [A] reach the value of 0.05 ML^{-1} ?

Ans. $$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$$

$k = 6\ min^{-1}$, $[A]_0 = 0.5$, $[A] = 0.05$, $t = ?$

$$t = \frac{2.303}{6}\log\frac{0.5}{0.05} = \frac{2.303}{6}\log 10 = 0.3838\ min$$

Q.16. The conversion of the molecules X to Y follows second order kinetics. If the concentration of X is increased to three times, how will it affect the rate of formation of Y ?

Ans. 9 times

Q.17. A first order reaction has a rate constant $1.15 \times 10^{-3}\ s^{-1}$. How long will 5 gram of this reactant take to reduce to 3 grams ?

Ans. $t = 444$ seconds

Q.18. $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$. If rate of formation of NO is 6×10^{-4} atm min^{-1}, calculate the rate of formation of H_2O.

Ans. 9.0×10^{-4} atm min^{-1}

Q.19. A first order reaction is 75% completed in 60 min. Find the half life of this reaction.

Ans. 30 mins.

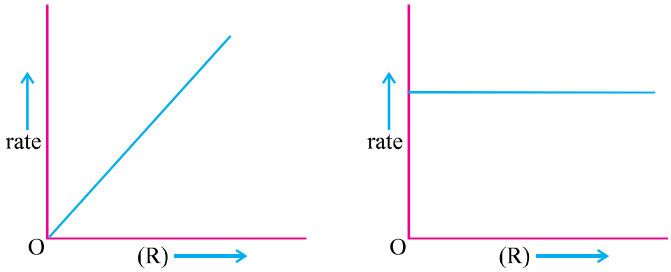
Q.20. The composition of a hydrocarbon follows the equation $K = (4.5 \times 10^{11}\ sec^{-1})\ e^{-28000K/T}$. Calculate the value of E_a.

Ans. 232.79 kJ/mol

Q.21. Consider a certain reaction A $\rightarrow$ Product with $K = 2.0 \times 10^{-2}\ s^{-1}$. Calculate the concentration of A remaining after 100 s, if the initial concentration of A is 1.0 mol L^{-1}.

Ans. [A] = 0.135 M

Q.22. Explain with an example, what is a pseudo first order raction ? The graphs (A and B) given below are plots of rate of reaction Vs concentration of the reactant. Predict the order from the graphs.



Q.23. Differentiate between :

(a) Average rate and instantaneous rate of a chemical reaction.

(b) Molecularity and order of reaction.

Q.24. Show that in case of first order reaction, the time required for 99.9% of the reaction to take place is about ten times than that required for half the reaction.

Q.25. For the reaction $NO_2 + CO \rightarrow CO_2 + NO$, the experimentally determined rate expression below 400 K is rate = $k[NO_2]^2$. What mechanism can be proposed for this reaction ?

Q.26. The half life period of a first order reaction is 60 min. What % will be left after 240 mins. ?

Ans. 6.25%

Q.27. Time for half change for a first order reaction is 25 min. What time will be required for 99% reaction ?

Ans. 166.16 mins.

SHORT ANSWER TYPE-II QUESTIONS

Q. 1. The rate constant for first order reaction is 60/s. How much time will it take to reduce the concentration of the reaction to 1/10 of its initial value ?

Ans.

$$t = \frac{2.303}{K} \log \frac{[R_0]}{[R]}$$

$$t = \frac{2.303}{\frac{1}{10}} \log \frac{[R_0]}{[R]}$$

$$t = \frac{2.303}{60} \log 10$$

$$t = \frac{2.303}{60}$$

$$= 3.38 \times 10^{-2}\ s^{-1}$$

Q. 2. The rate of most of reaction double when their temperature is raised from 298 K to 308 K. Calculate the activation energy of such a reaction.

Ans.
$$\log\frac{K_2}{K_1} = \frac{E}{2.303R}\frac{1}{T_1} - \frac{1}{T_2}$$

$$E_a = \frac{2.303 \times 8.314 \times 298 \times 308 \times 0.3010}{1000}$$

$$E_a = 52.89\ KJ/mol$$

Q. 3. A first order reaction takes 69.3 min for 50% completion. Set up on equation for determining the time needed for 80% completion.

Ans.
$$K = \frac{0.693}{t_{1/2}}$$

$$= \frac{0.693}{69.3}\ min$$

$$= 10^{-2}\ min^{-1}$$

$$T = \frac{2.303}{K}\log\frac{[R_0]}{[R]}$$

$$= \frac{2.303}{10^{-2}}\log 5$$

$$= 160.9\ min$$

Q. 4. The rate constant of a reaction is 1.2×10^{-3} sec^{-1} at 40° C. Calculate the energy of activation of the reaction.

Ans. $K_1 = 1.2 \times 10^{-3}\ sec^{-1}$ $\quad T_1 = 30 + 273 = 303\ K$

$K_2 = 2.1 \times 10^{-3}\ sec^{-1}$ $\quad T_2 = 40 + 273 = 313\ K$

Using,
$$\log\frac{K_2}{K_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$\Rightarrow$ $E_a = 44.13$ KJ mol^{-1}

Q. 5. The activation energy of a reaction is 94.14 KJ/mol and the value of rate constant at 40° C is 1.8×10^{-1} sec^{-1}. Calculate the frequency factor A.

Ans. Given, $E_a = 94.14 \times 10^3$ J mol^{-1}, T = 40 + 273 = 313 K, K = 1.8×10^{-1} sec^{-1}

By using,

$A = \text{antilog}\ (10.9635) = 9.194 \times 10^{10}$ sec^{-1}

Q. 6. The rate constant of a reaction at 500 K and 700 K are 0.02 s^{-1} and 0.07 s^{-1} respectively. Calculate the value of E_a and A.

Ans. 18.23 KJ mol^{-1}, 1.603

Q. 7. The rate constant of a reaction at 700 K and 760 K are 0.011 M^{-1} s^{-1} and 0.105 M^{-1} s^{-1} respectively. Calculate the value of Arrhenius parameters.

Ans. 2.824×10^{10}

Q. 8. The initial concentration of N_2O_5 in the first order reaction $N_2O_5 \rightarrow 2NO_2 + ½O_2$ was 1.24×10^{-2} mol L^{-1} at 318 K. The concentration of N_2O_5 after 60 minutes was 0.20×10^{-2} mol L^{-1}. Calculate the rate constant of the reaction at 318 K.

Ans.

Q. 9. The following data were obtained during the first order thermal decomposition of N_2O_5 at constant volume :

$$2N_2O_5 \rightarrow 2N_2O_4 + O_2$$

S. No.	Time per second	Total pressure (atm)
1	0	0.5
2	100	0.512

Calculate rate constant.

Ans. 4.98×10^{-4} sec^{-1}

Q. 10. A first order reaction is 20% complete in 20 minutes. Calculate the time taken for the reaction to go to 80% completion.

Ans. 144.3 minutes

Q. 11. For a first order reaction, calculate the ratio between the time taken to complete ¾ of the reaction and the time taken to complete half of the reaction.

Ans. Two

Q. 12. The following results have been obtained during the kinetics studies of the reaction :

$$2A + B \rightarrow C + D$$

Experiment	[A] mol L^{-1}	[B] mol L^{-1}	Initial rate of formation of D mol L^{-1} min^{-1}
I	0.1	0.1	6.0×10^{-3}
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-1}

Determine the rate law and the rate constant for the reaction.

Ans. Rate = K[A][B]

Q. 13. The rate of reaction triples when the temperature changes from 293 K to 313 K. Calculate the energy of activation of the reaction assuming that it does not change with temperature.

Q. 14. A first order reaction takes 40 m,ins for 30 decomposition. Calculate $t_{½}$.

Ans. 77.7 mins.

Q. 15. The decomposition of A into product has value of K as 4.5×10^3 sec^{-1} at 10° C and energy of activation 60 kJ/mol. At what temperature would K be 1.5×10^4 sec^{-1}.

Ans. 24° C

Q. 16. The rate of formation of NO is 3.6×10^{-3} mol L^{-1} sec^{-1}. Calculate the rate of disappearance of NH_3 and rate of formation of H_2O.

Ans. 3.6×10^{-3} Ms^{-1}, 5.4×10^{-3} Ms^{-1}

Q. 17. (a) Write rate law and order of the following reaction :

$AB + C_2 \rightarrow AB_2C + C$ (slow)

$AB_2 + C \rightarrow AB_2C$ (fast)

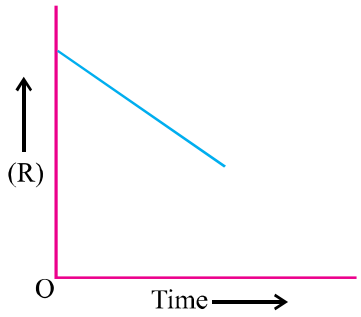
(b) Define energy of activation of a reaction.

(c) What is the relationship between rate constant and activation energy of a reaction ?

Ans. (a) Rate = $K[AB_2][C_2]$, Order = 1 + 1 = 2

(c) $K = Ae^{-E_a/RT}$

Q. 18. For a chemical reaction R $\rightarrow$ P, the variation in the concentration (R) vs time (t) plot is given :



(a) Predict the order of reaction.

(b) Write down its rate law.

(c) What is the slope of the curve ?

Q. 19. What do you understand by a first order reaction ? Show that for a first order reaction time required to complete a definite fraction of the reaction is independent of initial concentration.

Q. 20. In a pseudo first order reaction of hydrolysis of an ester in H_2O, the following results were obtained :

t/s	0	30	60	90
Ester (M/L)	0.55	0.31	0.17	0.085

(a) Calculate the average rate of reaction between the time interval 30 to 60 sec.

(b) Calculate the pseudo first order rate constant for the hydrolysis of ester.

Ans. (a) Average rate during 30-60 sec. $= \dfrac{0.17 - 0.31}{60 - 30} = 4.67 \times 10^{-3}$ mol L^{-1} sec^{-1}

(b) $$K_{30} = \frac{2.303}{t}\log\frac{[A]_0}{[A]} = \frac{2.303}{30}\log\frac{0.55}{0.31}$$

$$K_{60} = \frac{2.303}{60}\log\frac{0.55}{0.17}$$

$$K_{90} = \frac{2.303}{90}\log\frac{0.55}{0.085}$$

Average K = 1.98×10^{-2} sec^{-1}

Q. 21. Following reaction takes place in one step :

$$\mathbf{2NO + O_2 \rightarrow 2NO_2}$$

How will the rate of the reaction of the above reaction change if the volume of reaction vessel is diminished to 1/3 of its original volume ? Will there be any change in the order of reaction with reduced volume ?

Ans. $2NO + O_2 \rightarrow 2NO_2$

$dx/dt = K*[NO]_2[O_2]_1$

[Since it is one step.]

If the volume of reaction vessel is diminished to 1/3, conc. of both NO and O_2 will become 3 times, the rate of reaction increased 27 times in the order of reaction with the reduced volume.

Q. 22. The decomposition of NH_3 on platinum surface is a zero order reaction. What are the rate of production of N_2 and H_2 ? [K = 2.5×10^{-4}]

Ans. $2NH_3 \rightarrow N_2 + 3H_2$

$$-\frac{1}{2}\frac{d[NH_3]}{dt} = \frac{d[NH_2]}{dt} + \frac{1}{3}\frac{d[H_2]}{dt}$$

$$\frac{d[NH_3]}{dt} = \text{rate} = k \times [NH_3]^0$$

$$= 2.5 \times 10^{-4} \text{ mol } L^{-1} \text{ sec}^{-1}$$

$$\frac{d[N_2]}{dt} = -\frac{1}{2}\frac{d[NH_3]}{dt}$$

$$= \frac{1}{2} \times 2.5 \times 10^{-4} \text{ mol } L^{-1} \text{ sec}^{-1}$$

$$d[H_2] = -\frac{3}{2}\frac{d[NH_3]}{dt} = \frac{3}{2} \times 2.5 \times 10^{-4}$$

$$= 3.75 \times 10^{-44} \text{ mol } L^{-1} \text{ sec}^{-1}$$

$$\text{Rate} = -\frac{d[NH_3]}{dt} = k \times [NH_3]^0$$

$$= 2.5 \times 10^{-4} \text{ mol } L^{-1} \text{ sec}^{-1}$$

Rate of production of N_2 $= 2.5 \times 10^{-4}$ mol L^{-1} sec^{-1}

LONG ANSWER TYPE QUESTIONS

Q. 1. (a) Define order of reaction.

(b) Rates of reaction double with every 10° rise in temperature. If this generalization holds for a reaction in the temperature ranges 298 K to 308 K, what would be the value of activation energy for their reaction ? R = 8.314 J K^{-1} mol^{-1}.

Ans. (a) **Order of Reaction :** It is the sum of powers to which the conc. terms are raised in rate law expression.

(b) $$\log \frac{K_2}{K_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Here, $T_1 = 298$ K, $T_2 = 308$ K, R = K^{-1} mol^{-1}

$$\frac{K_2}{K_1} = 2$$

$$\log 2 = \frac{E_a}{2.303 \times 8.314}\left[\frac{1}{298} - \frac{1}{308}\right]$$

$$0.3010 = \frac{E_a}{2.303 \times 8.314}\left[\frac{10}{298 \times 308}\right]$$

$$E_a = \frac{0.3010 \times 2.303 \times 8.314 \times 298 \times 308}{10}$$

$$= 52898 \text{ J mol}^{-1}$$

$$= 52.898 \text{ KJ mol}^{-1}$$

Q. 2. (a) What are pseudo chemical reaction ? Give example.

(b) Rate constant K of a reaction varies with temperature 'T' according to the equation :

$$\log K = \log A - \frac{E_a}{2.303R}\left(\frac{1}{T}\right)$$

where E_a is the activation energy. When a graph is plotted for log K vs 1/T, a straight line with a slope of -4250 K is obtained. Calculate E_a for the reaction.

Ans. (a) $\text{Slope} = \dfrac{E_a}{2.303R} = -4250\ \text{K}$

So, $E_a = -2.303 \times R \times \text{Slope}$

$= -2.303 \times 8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times 4250$

$= 81375.3\ \text{J mol}^{-1}$

$= 81.375\ \text{KJ mol}^{-1}$

(b) The chemical reaction which look like higher order reaction but in real they follow lower order kinetics.

For example, $CH_3COOC_2H_5 \xrightarrow{H^+} CH_3COOH + C_2H_5OH$

excess

Rate $= K[CH_3COOC_2H_5]$

Order $= 1$

Q. 3. (a) Determine the units of rate constant for first and zero order reaction.

(b) Show that time required for the completion of 99% of the first order reaction is twice the 90% of completion of the reaction.

Ans. (a) $K = (\text{mol})^{1-n} L^{n-1} S^{-1}$

For zero order, $n = 0$

So, $K = (\text{mol})^{1-0} L^{0-1} S^{-1} = S^{-1}\ \text{mol}\ L^{-1}$

For first order, $n = 1$

$K = (\text{mol})^{1-n} L^{n-1} S^{-1}$

So, $K = (\text{mol})^{1-1} L^{1-1} S^{-1}$

$= S^{-1}$

$$t = \frac{2.303}{K}\log\frac{[A]_0}{[A]}$$

$[A]_0 = a$, $= 0.01\ a$

...(i)

For 90% completion of reaction,

...(ii)

Dividing equation (i) by equation (ii), we get

$$t(99\%) = 2 \times t(90\%)$$

Q. 4. (a) Define rate constant of reaction.

(b) A first order reaction takes 40 mins for 30% decomposition. Calculate $t_{½}$.

Ans. (a) **Rate constant :** It is the rate of chemical reaction when the concentration of reactant taken as unity at a given temperature.

(b) Let initial conc. = a

Conc. after 40 mins. =

$= 0.70\ a$

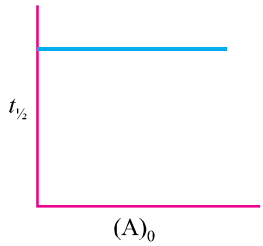
$$= \frac{2.303}{40} \times 0.1549$$

$$= 8.92 \times 10^{-3} \text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{K}$$

$$= \frac{0.693}{8.92 \times 10^{-3}} = 77.7 \text{ min}$$

Q. 5. (a) Determine the order of reaction and also determine the units of rate constant.



(b) The following data were given for thermal decomposition of SO_2Cl_2 at a constant volume :

$$SO_2Cl_2\,(g) \rightarrow SO_2\,(g) + Cl_2\,(g)$$

Exp.	Time/s	Total p/atm
1	0	0.5
2	100	0.6

Calculate the rate of the reaction when total pressure is 0.65 atm.

Ans. (a) First order reaction

$$K = \text{mol}^{1-n} L^{n-1} S^{-1}$$

$$n = 1$$

$$K = (\text{mol})^{1-1} L^{1-1} S^{-1}$$

$$= S^{-1}$$

(b)
$$k = \frac{2.303}{t} \log \frac{P_1}{(2P_1 - P_t)}$$

$$= \frac{2.303}{100} \log \frac{0.5}{(2 \times 0.5 - 0.6)}$$

$$= \frac{2.303}{100} \log \frac{0.5}{0.4}$$

$$= \frac{2.303}{100} \times 0.969 = 2.23 \times 10^{-3}\ s^{-1}$$

Now, Rate = $P_{SO_2Cl_2}$

Pressure of SO_2Cl_2 when total pressure = 0.65 atm

$$P_{SO_2Cl_2} = 2P_1 - P_t$$
$$= 2 \times 0.5 - 0.65$$
$$= 0.35 \text{ atm}$$
$$\text{Rate} = 2.23 \times 10^{-3} \times 0.55$$
$$= 7.8 \times 10^{-4} \text{ atm } S^{-1}$$

Q. 6. (a) The activation energy of a reaction is 100 kJ/mol. In the presence of catalyst the activation energy is decreased by 75%. What is the effect on rate constant of the reaction at 20° C ?

(b) $A + 2B \rightarrow 3C + 2D$

The rate of disappearance of B is 1×10^{-2} mol L^{-1} sec^{-1}. What will be (i) rate of reaction (ii) rate of change in the concentration of A and C ?

Ans. (a) 2.35×10^{13} times

$$[\textit{Hint :} \log \frac{K_2}{K_1} = \frac{E - E}{2.303RT} \Rightarrow \log \frac{K_2}{K_1} = \frac{75 \times 10^3}{2.303 \times 8.314 \times 293}]$$

(b) $(5 \times 10^{-3}, 5 \times 10^{-3}, 15 \times 10^{-3})$ M L^{-1} sec^{-1}

Q. 7. (a) For the reaction $2A + B \rightarrow A_2B$

the rate = $k[A][B]^2$ with $k = 2.0 \times 10^{-6}$ mol^{-2} L^2 sec^{-1}. Calculate the initial rate of reaction when [A] = 0.1 mol L^{-1}, [B] = 0.2 mol L^{-1}. Calculate the rate of reaction after [A] is reduced to 0.06 mol L^{-1}.

(b) (i) The activation energy for the reaction $2HI \rightarrow H_2 + I_2$ is 209.5 KJ/mol at 581 K. Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy.

(ii) The activation energy of a reaction is zero. Will the rate constant of the reaction depend upon temperature ? Give reason.

Ans. $K = Ae^{-E_a/RT}$ if $E_a = 0$, then $K = A$. Frequency factor (A) does not depend upon temperature, therefore, rate constant and rate does not depend on temperature.

Q. 8. The concentration of R in the reaction $R \rightarrow P$ was measured as a function of time and the following data is obtained :

[R] molar	1.0	0.75	0.40	0.10
t (in min)	0.0	0.05	0.12	0.18

Calculate the order of the reaction.

[*Hint :* Determine the rate of reaction at different intervals of time. It comes out to be constant. Hence, it is a zero order reaction.]

VALUE BASED QUESTIONS (4 Marks)

Q. 1. Food and dairy products get spoiled more quickly in summer. Therefore, use of refrigerator has became very common in almost every house. Sita, a class XII Chemistry student, suggested her mother to store milk and other dairy products in refrigerator and not in open on kitchen slab.

(a) Why Sita suggested her mother to store milk and dairy products in the refrigerator ?

(b) Mention the relationship to express how rate of reaction is related with temperature.

(c) What values are learnt by Sita's advice ?

(d) Name the food preservative used to prevent spoilage of food.

Q. 2. Ramesh tried his best to carry out the reaction between the pure hydrogen with pure oxygen but he failed. Mohan, a friend of Ramesh, suggested that the reaction must be carried out in the presence of Pt catalyst. As he placed platinum in the reaction mixture, the reaction took place explosively.

(a) Mention the role of catalyst in the above chemical reaction.

(b) What values are associated with the suggestion of Mohan ?

Define (c) activity and (d) selectivity of a catalyst.

Q. 3. Sudha's mother received a phone call on Monday morning from a close relative stating that three of them would be coming over for lunch. Sudha's mother noticed that she did not have enough curd to serve the guests. Sudha, a class XII chemistry student, suggested to her mother to take warm milk and keep it under direct sunlight and curdle it.

(a) Why do you think Sudha suggested the above method ?

(b) Will it be helpful if her mother followed Sudha's suggestion ?

(c) What values are associated with Sudha's suggestion ?

(d) Name the bacteria responsible for curdling of milk.